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(54) **Propylene-ethylene copolymer base resin composition for molding purposes**

(57) A molding composition comprises 57 to 62 wt% of a propylene-ethylene block copolymer containing 2 to 3 wt% ethylene and having a melt index (g/10 min at 230°C) of 40 to 45; 26 to 28 wt% of an ethylene-propylene copolymer rubber containing 70 to 80 wt% ethylene and having a Mooney viscosity, ML1+4(100°C), of 55 to 58; 2 to 3 wt% of high density polyethylene having a density in the range from 0.955 to 0.960 g/cm^3 and melt index (g/10 min at 190°C) of 18 to 22; and 10 to 12 wt% of talc having a mean particle size of 1.8 to 2.2 μm and a specific surface area of 36000 to 42000 cm^2/g; the composition having a density of 0.950 to 0.980 g/cm^3, a melt index (g/10 min at 230°C) of 13 to 18, a modulus of elasticity in bending of 11500 to 14000 kg/cm^2, and a coefficient of linear expansion 20-80°C of 7×10^{-5} to 10×10^{-5} cm/cm/°C.

This print takes account of replacement documents submitted after the date of filing to enable the application to comply with the formal requirements of the Patents Rules 1982.

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SPECIFICATION

Propylene-ethylene copolymer base resin composition for molding purposes

Background of the Invention

This invention relates to a propylene-ethylene copolymer base thermoplastic resin composition which is of use as a molding material and is particularly suited for bumpers and other exterior parts of automobiles.

In the automobile industry there is a growing tendency to employ plastics for exterior parts and accessories as an important means to meet both the demand for further reduction in weight and the demand for enlargement of the freedom of shaping and coloring. As a typical example, the bumpers are formed of plastics in recent automobiles of many models.

Plastics molding materials for automobile bumpers are required to be high in impact resistance and excellent in toughness. With this requirement considered, polypropylene and propylene-ethylene copolymers have attracted interest as the bumper materials. At the early stage of development a copolymer of propylene with a relatively small amount of ethylene (e.g. about 95/5 by weight) and a blend of polypropylene and ethylene-propylene rubber were used with particular attention to impact resistance. However, the bumpers formed of these polypropylene base materials are liable to be distorted by heat because the bumper materials are too soft and are considerably larger in the coefficients of linear expansion than the car body materials. It is possible to relieve the stress attributed to the difference of the linear expansion coefficients by longitudinally slidably supporting the bumper at bumper stays, but such a measure is unfavourable for the appearance of the car because the clearance between the bumper and the fender panel varies by about 10 mm as the temperature varies over a wide range.

As a propylene-ethylene copolymer base bumper material having a smaller coefficient of linear expansion, a blend of a propylene- ethylene rubber, high density polyethylene and talc has been developed recently. However, in various respects this resin composition is still unsatisfactory as a practical bumper material. First, the modulus of elasticity in bending is not sufficiently high. Second, scratch resistance is low because of the use of ethylene-propylene rubber which is low in Mooney viscosity. Thirdly, when the molding is painted the strength of adhesion of the paint film is at a barely acceptable level. Besides, this resin composition is relatively low in melt flow rate or melt index and, therefore, is not fully satisfactory in moldability.

Summary of Invention

It is an object of the present invention to provide an improved resin composition with a propylene-ethylene copolymer base, which is useful as a molding material for various articles including ones for outdoor uses and is excellent in all the properties required of automobile bumpers.

The present invention provides a resin composition useful as a molding material, which is a blend comprising (a) 57 to 62 wt% of a propylene-ethylene block copolymer in which the content of ethylene is from 2 to 3 wt% and of which the melt index (g/10 min) at 230°C is in the range from 40 to 45, (b) 26 to 28 wt% of an ethylene-propylene copolymer rubber in which the content of ethylene is from 70 to 80 wt% and of which the Mooney viscosity, ML1+4(100°C), is in the range from 55 to 58, (c) 2 to 3 wt% of high density polyethylene which has a density in the range from 0.955 to 0.960 g/cm³ and of which the melt index (g/10 min) at 190°C is in the range from 18 to 22, and (d) 10 to 12 wt% of talc having a mean particle size in the range from 1.8 to 2.2 μm and a specific surface area in the range from 36000 to 42000 cm²/g. As to physical properties, this resin composition shall satisfy the following requirements:

density: from 0.950 to 0.980 g/cm³;
melt index (g/10 min) at 230°C: from 13 to 18;
modulus of elasticity in bending: from 11500 to 14000 kg/cm²; and
coefficient of linear expansion over 20-80°C: from 7×10^{-5} to 10×10^{-5} cm/cm/°C.

Preferably, the ingredients are blended such that the surface glossiness of this resin composition becomes not lower than 55% when measured by the 60°-60° method according to JIS z 8741, which corresponds to ASTM D 523-53 T. ("JIS" stands for Japanese Industrial Standard.)

As will be understood from the above statement, the composition of the invention is a thermoplastic resin composition. This resin composition can be molded into various parts or articles, which may be for outdoor uses, by using conventional molding methods for thermoplastic resins. This resin composition is excellent in almost every aspect and particularly features high impact resistance, high modulus of elasticity in bending and a relatively small coefficient of linear expansion. Besides, this resin composition is sufficiently high in melt index and accordingly is excellent in moldability.

Therefore, a resin composition of the invention is very suitable as a molding material for automobile bumpers. In fact, automobile bumpers formed of this resin composition are very tough and sufficiently high in impact resistance and are satisfactory also in other aspects such as appearance, moldability, scratch resistance and paintability. Furthermore, these bumpers do not undergo significant heat distortion or thermal expansion since the resin composition has a fairly good thermal stability and is relatively small in the coefficient of linear expansion.

Such improvements on a physical properties of a propylene-ethylene copolymer base resin composi-

tion have been produced by optimizing the proportions of the four kinds of essential ingredients and, besides, by carefully and strictly specifying important characteristics of the respective ingredients.

At the start of our inventive studies, it was primarily intended to enhance the modulus of elasticity in bending of a propylene-ethylene copolymer base resin and to simultaneously decrease the coefficient of linear expansion of the same resin as a fundamental measure for producing automobile bumpers which are fairly little in distortion or expansion by the influence of varying environmental temperatures. Basically this purpose is accomplished by addition of an inorganic filler to a propylene-ethylene copolymer base resin, and in the present invention talc is judged to be the most suited for this purpose.

However, mere addition of talc results in great lowering of the impact resistance of the propylene-ethylene copolymer base resin, so that the resin becomes useless as a bumper material. The addition of a rubber component is necessary as a means to effectively compensate for such lowering of the impact resistance. However, utmost care must be taken in selecting the rubber component and determining the amount of its addition while considering the effects of talc too, because the addition of a rubber to a propylene-ethylene copolymer base resin is a cause of lowering of the modulus of elasticity of the resin.

Besides, attention has been paid to the fact that the inclusion of a rubber component in the resin composition is rather unfavourable for the appearance, hardness and scratch resistance of the modling surfaces, so that the moldings such as bumpers are liable to suffer from surface defects such as flow marks and stick slips. The selection of the rubber component is made with due consideration of this matter, and an adequate amount of high density polyethylene of a suitable class is incorporated besides talc and ethylene-propylene copolymer rubber in order to minimize the unfavourable influence of the rubber component on the quality of the molding surfaces. The glossiness of the molding surfaces and the strength of adhesion of paint film to the molding surfaces are also significantly affected by the amount and properties of the rubber component. This matter too has been taken into consideration in devising the improved resin composition. One of the effects of the addition of high density polyethylene is an improvement in the glossiness of the molding surfaces.

Description of the Preferred Embodiments

In a resin composition according to the invention, a primary component is a propylene-ethylene copolymer which is required to be a block copolymer. Homopolymer of propylene and random copolymers of propylene with ethylene are unsuitable because they do not effectively contribute to the enhancement of the impact resistance of the resin composition. Also it is required that the content of ethylene in the propylene-ethylene copolymer be in the range from 2 to 3 wt%. When the ethylene content is less than 2% it is difficult to obtain a resin composition which is sufficiently high in impact resistance. On the other hand, as the ethylene content exceeds 3% the resin composition becomes lower in scratch resistance and also in glossiness. Furthermore, it is important that the melt flow rate of the propylene-ethylene copolymer at 230°C be in the range from 4o to 45 g/10 min. The resin composition will be unsatisfactory in moldability when the melt index of this copolymer is below 40 and becomes lower in impact resistance as the melt index of the copolymer exceeds 45.

In a resin composition of the invention, a propylene-ethylene block copolymer of the above described class must occupy from 57 to 62% of the composition by weight. This range is specified mainly because the resin composition becomes lower in the modulus of elasticity in bending and in impact resistance when the amount of this copolymer is either less than 57% or more than 62%. Besides, when the amount of this copolymer is less than 57% the strength of adhesion of paint film to a molding of the resin composition will not always high enough.

The second major component of the resin composition is an ethylene- propylene copolymer rubber, which must be a binary ethylene-propylene rubber classified as EPM. Other synthetic rubbers such as ethylene-propylene-nonconjugated diene copolymer rubber (EPDM), isoprene rubber, butyl rubber and butadiene rubber are not suitable for various reasons including insufficient contribution to the enhancement of impact resistance and tendencies to the appearance of flow marks on the moldings. It is necessary to use an ethylene-propylene copolymer rubber containing 70 to 80 wt% of ethylene. If the ethylene content in the rubber is less than 70% the resin composition will be insufficient in scratch resistance. When the ethylene content in the rubber is more than 80% the resin composition becomes lower in impact resistance. Also it is required that the Mooney viscosity, ML1+4(100°C), of the ethylene-propylene rubber be in the range from 55 to 58. If a mixture of two or more kinds of ethylene-propylene rubbers is used it suffices that an average of the Mooney viscosity values of the respective rubbers falls in this range. If the Mooney viscosity of the ethylene- propylene rubber is lower than 55 the scratch resistance of the resin composition will be insufficient, and the strength of adhesion of paint film to the moldings will be so low that delamination may occur. If the Mooney viscosity of the rubber is higher than 58, flow marks will appear on the moldings and the glossiness will significantly lower.

The content of an ethylene-propylene copolymer rubber in the resin composition must be within the range from 26 to 28% by weight. The resin composition becomes lower in impact resistance when the content of the rubber is either less than 26& or more than 28%. Besides, when the content of the rubber is less than 26% the strength of adhesion of paint film will be insufficient, and when the content of the rubber is more than 28% flow marks will appear on the moldings.

Another plastic component of the resin composition is high density polyethylene having a density of

from 0.955 to 0.960 g/cm³. It is required that the melt flow rate of the high density polyethylene at 190°C be in the range from 18 to 22 g/10 min. If the melt index of the high density polyethylene is below 18 the resin composition will be insufficient in glossiness and will suffer from the appearance of flow marks. The use of polyethylene higher than 22 in flow index is unfavourable for impact resistance of the resin composition.

The content of high density polyethylene in the resin composition must be within the range from 2 to 3% by weight. When the content of polyethylene is less than 2% a favourable effect of polyethylene on the glossiness remains insufficient. If the content of polyethylene is more than 3%, the strength of adhesion of paint film to the moldings will become lower.

In the present invention, talc used as an inorganic filler is required to have a mean particle size in the range from 1.8 to 2.2 μ and a specific surface area in the range from 36000 to 42000 cm²/g. If the talc is smaller than 1.8 μm in mean particle size, very intense kneading is needed in preparing the resin composition with good dispersion of talc. On the other hand, the use of talc larger than 2.2 μm in mean particle size is not highly effective for enhancing the modulus of elasticity in bending of the resin composition and results in relatively low impact resistance and scratch resistance of the resin composition.

The content of talc in the resin composition must be within the range from 10 to 12% by weight. If the content of talc is less than 10% the modulus of elasticity in bending will become lower and the coefficient of linear expansion will not lower to a desired extent. If the content of talc is more than 12% the resin composition will become lower in impact resistance and will suffer from unsatisfactory appearance when molded.

In addition to the above described essential ingredients, a resin composition according to the invention may optionally contain any of the additives commonly used in conventional thermoplastic resin compositions. For example, an antioxidant, an ultraviolet absorbing agent and/or a pigment may be added according to the need.

A resin composition according to the invention can easily be prepared by uniformly blending the above described ingredients. It is preferable to employ such a blending method as causes melting of the propylene-ethylene block copolymer and/or the rubber. For accomplishment of uniform blending it is most suitable to use a twin screw keader-extruder though a single-screw extruder or any other suitable machine can alternatively be used. Usually the uniformly blended resin composition is extruded into the form of pellets.

Molding of a resin composition of the invention can be performed by various molding methods used for molding conventional thermoplastic resins. For molding of this resin composition into automobile bumpers it is suitable to employ either an injection molding method or a stamping method. The bumpers formed of this resin composition can be painted in a desired color by using a conventional method. For example, a polyurethane base paint may be applied preceded by cleansing with a suitable solvent such as 1,1,1- trichloroethane vapor or by a low-temperature plasma treatment.

Examples

As Examples 1 and 2, two kinds of resin compositions according to the invention were prepared by blending a propylene-ethylene block copolymer, an ethylene-propylene copolymer rubber (EPR), high density polyethylene and talc. The particulars of the raw materials and the proportions of the blended materials are shown in Table 1.

As references 1-14 for comparison, thirteen kinds of propylene- ethylene copolymer base resin compositions not in accordance with the invention and one kind of a propylene homopolymer base resin composition (Reference 13) were prepared as shown in Table 1.

The talc used in Examples 1 and 2 and in most of References (2.0 μm in mean particle size) had a specific surface area of 40000 cm²/g, and the talc used in Reference 6 (7.0 μ in mean particle size) had a specific surface area of 10000 cm²/g.

TABLE 1

	Propylene-ethylene Copolymer				Rubber				High Density Polyethylene			Talc	
	Type	Amount (wt%)	Melt Flow Rate (g/10min)	Ethylene Content (wt%)	Kind	Amount (wt%)	Mooney Viscosity (ML1+4 (100°C))	Ethylene Content (wt%)	Amount (wt%)	Melt Flow Rate (g/10min)	Density (g/cm³)	Amount (wt%)	Mean Particle Size (μm)
Ex. 1	block	62	44	3	EPR	26	57	75	2	20	0.957	10	2.0
Ex. 2	block	57	44	3	EPR	28	57	75	3	20	0.957	12	2.0
Ref. 1	block	62	35	3	EPR	26	57	75	2	20	0.957	10	2.0
Ref. 2	block	62	44	5	EPR	26	57	75	2	20	0.957	10	2.0
Ref. 3	block	62	44	3	EPR	26	70	75	2	20	0.957	10	2.0
Ref. 4	block	62	44	3	EPR	26	18	75	2	20	0.957	10	2.0
Ref. 5	block	62	44	3	EPR	26	57	75	2	5	0.960	10	2.0
Ref. 6	block	62	44	3	EPR	26	57	75	2	20	0.957	10	2.0
Ref. 7	block	65	44	3	EPR	23	57	75	2	20	0.957	10	2.0
Ref. 8	block	55	44	3	EPR	33	57	75	2	20	0.957	10	2.0
Ref. 9	block	55	44	3	EPR	26	57	75	2	20	0.957	17	2.0
Ref. 10	block	55	44	3	EPR	26	57	75	9	20	0.957	10	2.0
Ref. 11	block	64	44	3	EPR	26	57	75	0	-	-	10	2.0
Ref. 12	block	65	44	3	EPR	26	57	75	2	20	0.957	7	2.0
Ref. 13	homo	62	44	0	EPR	26	57	75	2	20	0.957	10	2.0
Ref. 14	block	62	44	3	EPDM	26	57	75	2	20	0.957	10	2.0

In every Example and in every Reference, 0.6 part by weight of antioxidant (n-octadecyl-β-(4'-hydroxy-3', 5'-di-tert-butyl phenol) propionate), 0.3 part by weight of ultraviolet absorbing agent (bis(2,2,6,6-tetra-methylpiperidyl)sebacate) and 0.5 part by weight of carbon black were added to 100 parts by weight of the blend of the essential ingredients.

The physical properties of the resin compositions of these Examples and References were as shown in Table 2.

The melt flow rate (melt index) was measured by the method according to JIS K 7210 at 230°C for the propylene-ethylene block copolymers, polypropylene and the resin compositions and at 190°C for high density polyethylenes. The density was measured in accordance with JIS K 7112. The modulus of elasticity in bending was measured by the method according to JIS K 7203. The test pieces were 3 mm in thickness and 48 mm in span, and the test speed was 1 mm/min. The coefficient of linear expansion was measured by the method according to ASTM D 696. The test pieces were 4 mm by 12.7 mm rectangular

and 100 mm long. The surface glossiness was measured by the 60°-60° method according to JIS Z 8741. The Izod impact test was in accordance with JIS K 7110. To find a mean particle size of talc, the particle size distribution was measured by the light transmission method in the liquid phase sedimentation method to obtain a cumulative distribution curve. The mean particle size value in Table 1 refers to a particle diameter at the 50% point on the cumulative distribution curve. The specific surface area of talc wa measured by the constant pressure air permeation method. Each sample for measuring the peel strength of paint film was prepared by the steps of applying a primer to a flat surface of a molding of the resin composition, baking the applied primer at 90°C for 20 min, applying a melamine-alkyd resin base paint as a top coat and then baking the top coat at 120°C for 30 min. In the peel test, a 10 mm width of the paint film was pulled in the -180° direction at a width of the paint film was pulled in the -180° direction at a rate of 20 mm/min.

TABLE 2

	Melt Flow Rate	*Density*	*Modulus of Elasticity in Bending*	*Coefficient of Linear Expansion (20-80°C)*	*Glossiness (60°-60°)*	*Izod Impact Value (40°C)*	*Peel Strength of Paint Film*
	(g/10min)	*(g/cm³)*	*(kg/cm²)*	*(cm/cm/°C)*	*(%)*	*(kg- cm/cm)*	*(kg/cm)*
Ex. 1	16	0.958	12500	9.0×10^{5}	66	7.2	0.9
Ex. 2	15	0.975	13800	7.8×10^{-5}	56	6.0	0.8
Ref. 1	11	0.958	12700	9.0×10^{-5}	50	7.5	0.8
Ref. 2	16	0.958	10500	9.0×10^{-5}	52	8.2	1.0
Ref. 3	13	0.958	12700	9.0×10^{-5}	30	10.0	1.2
Ref. 4	17	0.958	12200	9.0×10^{-5}	70	6.5	0.4
Ref. 5	10	0.958	12500	9.0×10^{-5}	20	10.0	0.5
Ref. 6	16	0.958	13200	9.0×10^{5}	50	4.0	0.6
Ref. 7	19	0.958	14500	11×10^{5}	40	4.0	0.8
Ref. 8	14	0.958	9200	6×10^{5}	72	>30	1.0
Ref. 9	14	1.025	20200	5×10^{5}	43	3.0	0.6
Ref. 10	13	0.960	11000	10×10^{5}	74	7.5	0.3
Ref. 11	17	0.957	12600	9.0×10^{-5}	50	7.2	1.1
Ref. 12	18	0.940	11200	11×10^{5}	67	8.0	0.9
Ref. 13	16	0.958	12800	9.0×10^{-5}	69	4.0	0.9
Ref. 14	16	0.958	12700	9.0×10^{-5}	40	8.0	0.6

CLAIMS

1. A resin composition useful as a molding material, which is a blend comprising:

57 to 62 wt% of a propylene-ethylene block copolymer in which the content of ethylene is from 2 to 3 wt%, the melt index (g/10 min) of said copolymer at 230°C being in the range from 40 to 45;

26 to 28 wt% of an ethylene-propylene copolymer rubber in which the content of ethylene is from 70 to 80 wt%, the Mooney viscosity, ML1+4(100°C), of said rubber being in the range from 55 to 58;

2 to 3 wt% of high density polyethylene having a density in the range from 0.955 to 0.960 g/cm³, the melt index (g/10 min) of said polyethylene at 190°C being in the range from 18 to 22; and

10 to 12 wt% of talc having a mean particle size in the range from 1.8 to 2.2 μm and a specific surface

area in the range from 36000 to 42000 cm^2/g;

the density of the resin composition being in the range from 0.950 to 0.980 g/cm^3, the melt index (g/10 min) of the resin composition at 230°C being in the range from 13 to 18, the modulus of elasticity of the resin composition in bending being in the range from 11500 to 14000 kg/cm^2, and the coefficient of linear exansion of the resin composition over 20-80°C being in the range from 7×10^5 to 10×10^5 cm/cm/°C.

2. A resin composition according to Claim 1, wherein the surface glossiness of the resin composition measured by the method defined herein is not lower than 55%.

3. An automobile bumper formed of a resin composition according to Claim 1.

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